



Boron-doped porous carbon boosts electron transport efficiency for enhancing Fenton-like oxidation capacity: High-speed driving of Fe (III) reduction

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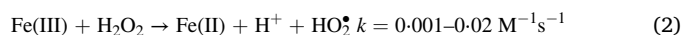
Fe(III)/Fe(II) redox cycle
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ABSTRACT

Herein, Fenton-like cocatalysts with sufficient activity and stability were developed to accelerate the Fe(III)/Fe(II) redox cycle, thereby enhancing the oxidation capacity of Fe(III)/H₂O₂ system. A porous engineering coupled with heteroatom doping strategy was adopted to prepare high-performance cocatalysts represented by boron-doped porous carbon (BPC). A small amount of BPC input (0.04 g/L) drives the efficient degradation of pollutants in Fe(III)/H₂O₂ system via •OH-dominated radical pathway. Based on characterization results, the doping of boron species optimizes the pore structure of cocatalysts and improves their co-catalytic activity. Meanwhile, boron content increase steers the reduction of Fe(III) in BPC/Fe(III)/H₂O₂ system through an “expressway” with higher electron transport efficiency. Theoretical calculations suggested the “electron porter” effect of BCO₂ on BPC to produce free Fe(II) for H₂O₂ activation. The continuous-flow device using BPC as a membrane component has excellent performance in purifying micro-polluted water. This study provides a novel co-catalytic Fenton-like method for water remediation.

1. Introduction

Fenton process, with the merits of high efficiency and simple operation, is the most useful modern oxidation technique for water pollution control [1–3]. Under acidic circumstances, Fe(II) can react with hydrogen peroxide (H₂O₂) to generate hydroxyl radicals (•OH, E₀ = 2.80 V/NHE) (Eq. 1), which is a powerful weapon to degrade persistent contaminants and inactivate pathogens. [4–7]. However, the main obstacle in front of the development of Fenton process is the Fe species transition from Fe(III) to Fe(II) because of its sluggish kinetics (Eq. 2) [8, 9]. Due to untimely electronic replenishment, sustainable and efficient oxidation performance cannot be achieved.



To overcome this issue, the primary concern is to accelerate the reduction of Fe(III). In recent years, heterogeneous cocatalysts have attracted increasing attention due to their recyclability, structural adjustability and strong reducibility [10]. Xing et al. found that zero-valent metals (e.g., Mo⁰ [11]) and metal sulfides/oxides (e.g., MoS₂ [12–15], WS₂ [16], and MoO₂ [17]) had good capacity to boost the Fe(III)/Fe(II) redox cycle. To avoid metal ion leaching, scholars have also developed a series of metal-free cocatalyst materials, such as multi-walled carbon nanotubes [18,19], crystalline boron [20] and black red phosphorus [21]. Carbon-based materials stand out from the aforementioned materials owing to better environmental friendliness [10], but their co-catalytic activity is still expected to be further improved.

Heteroatom doping tactics are the effectual measures to modify the co-catalytic characteristics of carbon materials [22,23], among which boron doping has definitely attracted scientists' attention in the design

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of metal-free catalysts [24–26]. Boron ($\chi_B = 2.04$) has a lower electronegativity than carbon ($\chi_C = 2.55$), exhibiting a lower Fermi level and a tendency to readily lose electrons [26]. The relatively small atomic radius of boron makes it easy to enter the carbon lattice and replace sp^2 and sp^3 structures, thus improving the electronic conductivity of carbon materials [27]. Density functional theory (DFT) calculations further demonstrate that boron doping can induce a polarization phenomenon on the carbon surface, promoting electrostatic and ion- π interactions between the material surface and solution ions [28]. Considering these properties, boron-doped carbon materials hold promise as excellent co-catalysts to enhance the oxidation ability of Fenton-like systems. Although boron-containing materials (such as amorphous/crystalline boron and boron carbide [29]) have been reported to accelerate Fe(III) reduction, there is currently no research on the use of boron-doped carbon materials as Fenton-like cocatalysts.

For the co-catalytic Fe(III) reduction mechanism, the B-B bond on the surface of crystalline boron can directly provide electrons to Fe(III), releasing homogeneous Fe(II) for H_2O_2 activation [20,30]. Different from the boron system, the interfacial electron transfer caused by the complexation of iron ions with cocatalysts is the key to the reduction of Fe(III) in carbon materials (such as carbon nanotubes [18], hydrophilic mesoporous carbon [31] and fullerol [32]) co-catalytic systems, and the activation of H_2O_2 happens on the surface of carbon materials. Containing both B and C atoms, boron carbide (B_4C) enhances the reduction of Fe(III) by H_2O_2 by increasing the redox potential of Fe(III) [29]. Obviously, different co-catalytic principles are involved in different boron-based and carbon-based cocatalysts, which is worth considering whether the reduction pathway of Fe(III) in the corresponding systems can be regulated by adjusting the proportion of carbon and boron in the materials. Therefore, it is very meaningful to study the influence of boron doping on the co-catalytic mechanism modulation of carbonaceous cocatalysts.

Micro-morphological structure control is another approach to endow material with fascinating properties. Motivated by the observation that the self-assembly process amongst precursors might result in the creation of distinct three-dimensional porous morphologies via intense hydrogen bonding reactions [33], we explored the potential of combining porous engineering with boron doping to create innovative cocatalysts. Consequently, boron-doped porous carbon materials (BPC) with optimized carbon skeleton structure were synthesized by a one-step carbonization method based on the self-assembly reaction between boron-containing precursors [34–36]. The involvement of BPC preeminently elevated the oxidation capability of Fe(III)/ H_2O_2 system towards diverse organic contaminants. Combined with experimental and theoretical calculation results, the role of boron doping for tailoring co-catalytic activity and Fe(III) reduction pathway involved in BPC/Fe(III)/ H_2O_2 system was systematically evaluated, and the primary oxidation mechanism was identified. Finally, the successful attempt of BPC co-catalytic membrane in continuous flow experiments verified its feasibility in practical water treatment. This study constructed a novel BPC/Fe(III)/ H_2O_2 oxidation system and provided new insights into Fe(III) reduction mechanism modulation in heteroatom-doped carbon material assisted Fenton-like systems.

2. Experimental section

2.1. Preparation of BPC cocatalyst

A typical procedure for synthesizing BPC cocatalyst is listed as follows. First, a certain amount of glucose (0.01 mol), sodium bicarbonate (0.02 mol) and 30 mL of water were added into a 50 mL beaker and stirred in a 100 °C water bath. After the solid is completely dissolved, a certain proportion of boric acid (0 mmol, 10 mmol, 15 mmol, 20 mmol, 30 mmol) was added. About two hours later, the mixture was collected and transferred into a combustion boat. Then, the combustion boat was placed into a tube furnace with the protection of N_2 atmosphere, which

was further pyrolyzed at 900 °C for 2.0 h to obtain BPC composites (heating rate: 5 °C/min). Subsequently, the sample after natural cooling was washed repeatedly with ethanol and deionized water via suction filtration. Finally, the target BPC cocatalyst was collected after drying in a vacuum oven. The prepared cocatalysts are referred to as PC, BPC-10, BPC-15, BPC-20, and BPC-30, respectively, depending on the molar amount of boric acid added to the precursor. The precursor of BPC-30 pyrolyzed at different temperatures (i.e., 600 °C, 700 °C, 800 °C and 900 °C) were donated as BPC₆₀₀, BPC₇₀₀, BPC₈₀₀ and BPC₉₀₀.

2.2. Experimental procedures

In this study, all experiments were conducted in a 100 mL beaker, stirred using a stirrer at 500 rpm to maintain homogeneity during the reaction. Typically, pollutants (e.g., caffeine (CAF), sulfamethoxazole (SMX), paracetamol (PCM), ibuprofen (IBP), naproxen (NPX), carbamazepine (CBZ) and nitrobenzol (NB), Table S1) are degraded by adding a certain amount of cocatalyst (for boosting the iron ion cycle), ferric nitrate solution (5.0 mM) and H_2O_2 (30%) into 50 mL of pollutant solution (10.0 mg/L). If not stated otherwise, the temperature was controlled at 25 °C, and the pH of the solution had been adjusted to 4.0 in advance using nitric acid and sodium hydroxide. At specific time intervals during the reaction, 1.0 mL of the sample was withdrawn and filtered using a 0.22 μ m film. Then, the reaction was quenched by adding 0.5 mL of methanol. Assays of organic compounds in samples were conducted using high-performance liquid chromatography (HPLC, Shimadzu Essentia LC-16, Japan) with a C18 column (WondaSil C18-WR 5 m, 4.6×15 cm), detailed test conditions are provided in Table S2.

2.3. Characterizations and analytical methods

Elemental composition and chemical valence state information of different cocatalysts were obtained by X-ray photoelectron spectroscopy (XPS) of Thermo Scientific K-alpha under Al K α radiation ($h\nu = 1486.6$ eV). Raman spectra of samples were obtained using a miniature Raman spectrometer (Renishaw inVia, UK) equipped with laser excitation at 633 nm. The specific surface area, pore volume and pore distribution of the samples were determined by physical adsorption of N_2 at 77 K on an auto-adsorption system (Auto Chem II 2920, Micromeritics, Inc., USA). The morphology of the prepared materials was observed by field emission scanning electron microscopy (FESEM, FEI Quanta 400 F, the Netherlands). The crystal structure of cocatalysts was analyzed by an X-ray diffractometer equipped with Cu K α radiation (Rigaku UltimaIV, Japan). The Fourier transform infrared spectrometer (FTIR, Bruker EQUINOX 55) was used to gain the functional group information of cocatalysts. The concentrations of free ferrous ions and total free iron species were detected by the 1,10-phenanthroline method using a 752 G UV-visible spectrophotometer (INESA 752 G, Shanghai) [37]. Modified ammonium metavanadate spectrophotometric method was used to measure the H_2O_2 concentration in the solution [38]. Electrochemical analysis was performed on an electrochemical workstation (CHI 660E, CH Instrument, China) with a three-electrode cell system. More experimental details are presented in the Supporting Information.

3. Results and discussion

3.1. Morphology and co-catalytic oxidation behaviors of BPC

As shown in Figs. 1a-b, the overall morphology of the BPC-30 material reflected a rough, micron-sized chip with densely spaced holes on the surface. The staggered three-dimensional (3D) internal channels might be attributed to the strong hydrogen-bonding interactions between boric acid, sodium bicarbonate and water molecules, which triggered the self-assembly reaction and formed the pore-crosslinked stereo structure during the carbonization of precursors [34–36]. Additionally, the elements mapping analysis (Figs. 1c-f) showed that boron

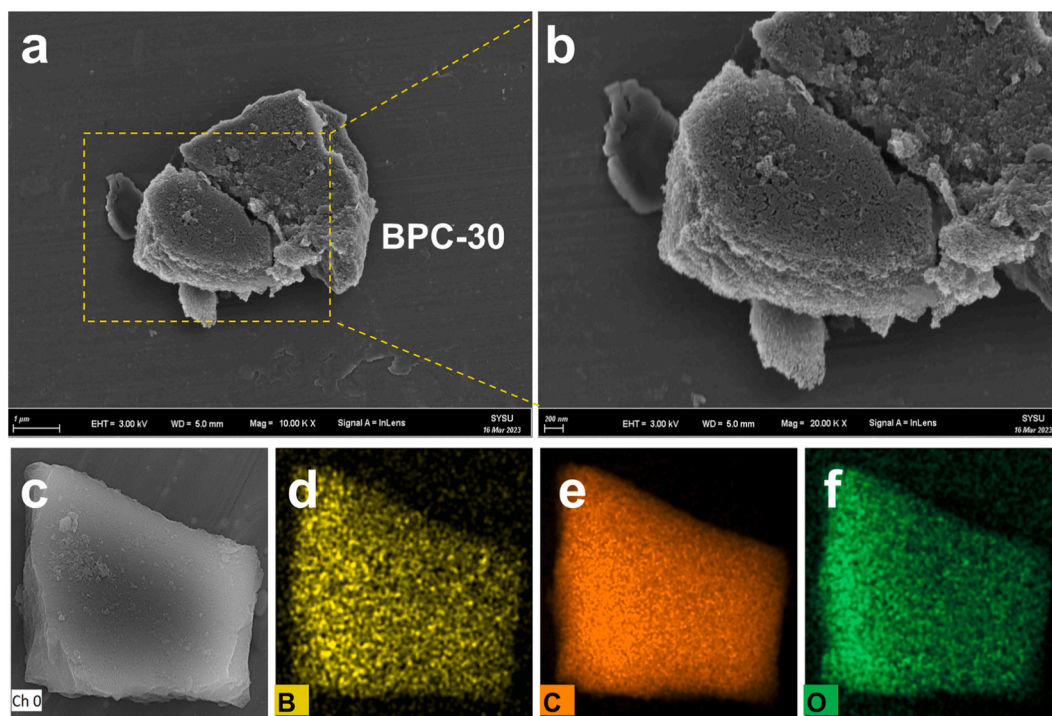


Fig. 1. SEM images of BPC-30: Mag = 10.00 K X (a), Mag = 20.00 K X (b); Element mapping images of BPC-30: sample (c), B (d), C (e) and O (f).

atoms are evenly distributed on BPC-30. The aforementioned findings indicated that the boron-doped porous carbon material was successfully synthesized.

To assess the efficacy of BPC cocatalyst in improving the oxidation performance of Fe(III)/H₂O₂ system, degradation experiments were carried out selecting caffeine (CAF) as the model pollutant. As shown in Fig. 2a, sole BPC could not effectively activate H₂O₂ and only ~10% of CAF was adsorbed by BPC. Likewise, Fe(III)/H₂O₂ system had essentially little impact on the degradation of CAF at pH 4.0. Of note, after adding BPC (0.04 g/L), CAF was completely degraded within 30 min at a reaction constant rate (k_{obs}) of $(1.30 \pm 0.20) \times 10^{-1} \text{ min}^{-1}$ (Fig. 2a). The great improvement in CAF removal indicated that BPC manifests a remarkable co-catalytic capacity to boost the cycle of Fenton-like reaction for the oxidation of pollutants. The effects of BPC, Fe(III) and H₂O₂ concentrations on CAF elimination were then analyzed under diverse experimental settings. It was evident that the CAF degradation rate increased to varying degrees as the concentration rose (Figs. 2b-d). By modelling experimental data using the pseudo-first-order kinetics model (Figure S1), the total rate equation of CAF degradation in BPC/Fe(III)/H₂O₂ system was obtained, displayed as Eq. 3. The more significant reaction order of H₂O₂ concentration suggested that it had a rather considerable impact on the ability to degrade CAF.

$$v = -\frac{dc}{dt} = 3.6060 \times 10^{-2} [\text{BPC}]_0^{0.3666} [\text{Fe(III)}]_0^{0.5492} [\text{H}_2\text{O}_2]_0^{0.6341} \quad (3)$$

Next, the influence of pH (3.0–7.0) on the oxidation capacity of BPC/Fe(III)/H₂O₂ system was investigated. As displayed in Figure S2, the zeta potential of BPC decreases with increasing pH and the isoelectric point is between pH 1.2 and 2.0, implying BPC is negatively charged in the pH range of 3.0–7.0. Fig. 2e showed BPC/Fe(III)/H₂O₂ system maintained a high level of oxidation activity at acidic conditions (i.e., pH 3.0 and 4.0), which was able to completely degrade CAF in 60 min. Interestingly, pH 4.0 provided the best performance, consistent with previous studies [9, 23]. It can be explained by the fact that an appropriately raised pH facilitates the interaction between positively charged Fe(III) species and BPC owing to the enhanced electrostatic attraction. With the weakening of the acidity, only ~50% of CAF was eliminated after 60 min at pH 5.0,

and BPC/Fe(III)/H₂O₂ system had negligible oxidation capacity under neutral circumstances due to the hydrolytic inactivation of Fe(III) species.

The general applicability, anti-interference ability and stability of BPC/Fe(III)/H₂O₂ system were further focused. Fig. 2f demonstrated that a wide array of pollutants (e.g., CAF, NPX, CBZ, SMX, PCM and IBP) could be effectively removed within 30 min, indicating BPC/Fe(III)/H₂O₂ system exhibited excellent non-selective oxidation capabilities for diverse contaminants removal. Fig. 2g illustrates the effect of coexisting anions and humic acids on the elimination of CAF in BPC/Fe(III)/H₂O₂ system. The oxidation efficiency was marginally decreased by the addition of chloride (Cl⁻), bicarbonate (HCO₃⁻) and humic acid, which could be attributed to the formation of reactive species with low redox potential or the competitive consumption of reactive oxygen species (ROS) during reactions [39]. However, CAF degradation was significantly inhibited in the presence of dihydrogen phosphate (H₂PO₄⁻), which was attributed to that H₂PO₄⁻ captured Fe(III) ions to result in the ineffective activation of H₂O₂ [40]. CAF decomposition by BPC/Fe(III)/H₂O₂ system in different water matrices (including tap water, surface water and WWTP effluent from the secondary sedimentation tank, the corresponding water quality parameters are listed in Table S3) was further examined. The removal rate of CAF only showed a small decrease and it can still reach more than 90% after 60 min in all types of waters (Fig. 2h), which illustrates the viability of using BPC/Fe(III)/H₂O₂ system for actual water treatment. Cyclic tests were used to evaluate the reusability of the BPC cocatalyst. As shown in Fig. 2i, most of CAF (~90%) could still be removed after a 4-hour cycle, demonstrating its long-term co-catalytic activity.

3.2. Effect of boron doping on the optimized cocatalyst structure and activity

Initially, XPS was used to examine the element composition of as-prepared PC and BPC with different boron doping amounts (i.e., BPC-10, BPC-15, BPC-20 and BPC-30). As shown in Figure S5, the boron content in the cocatalyst increased accordingly with the increase of boric acid dosage in the preparation process. Four peaks were observed in the

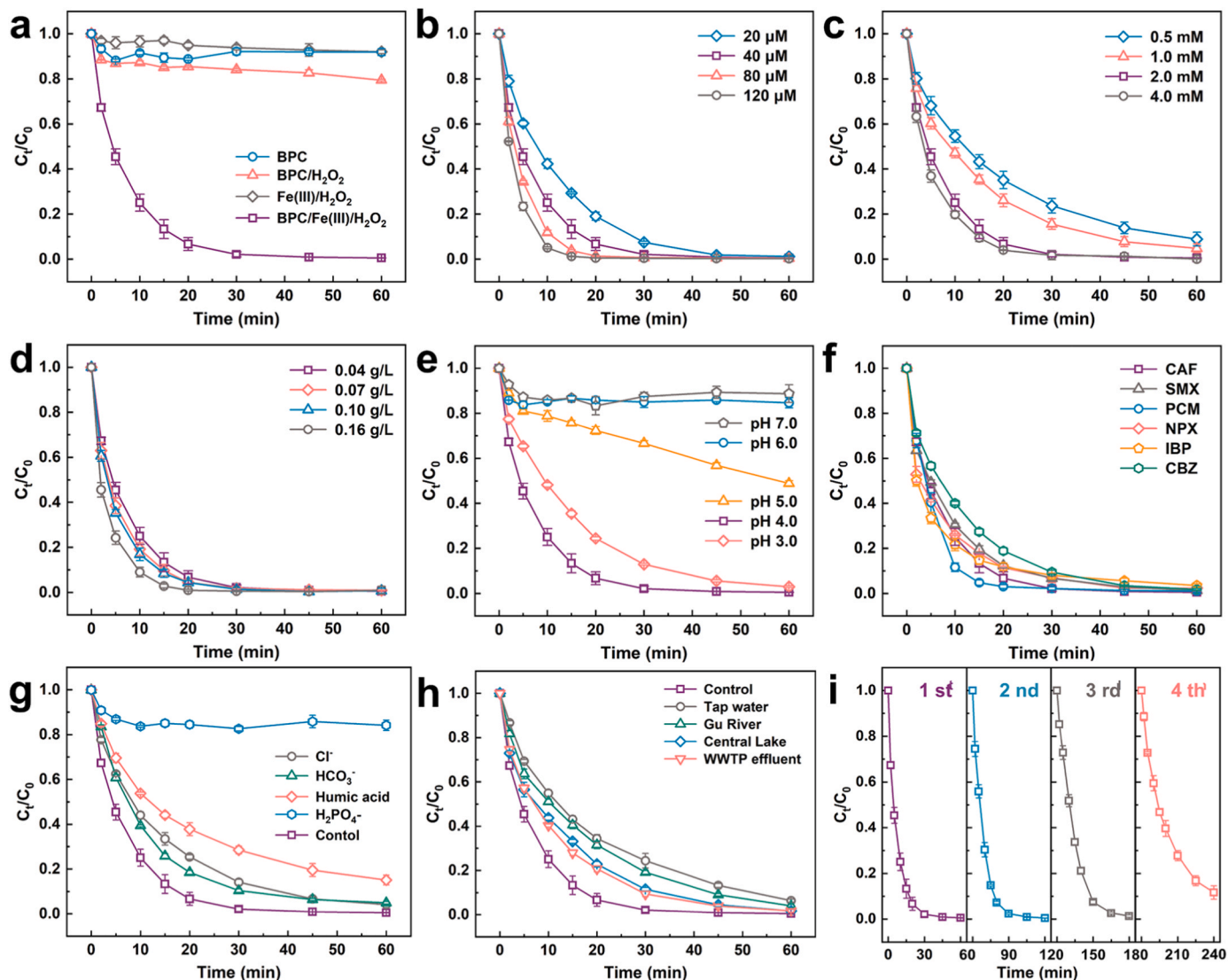


Fig. 2. (a) CAF removal by sole BPC, BPC/H₂O₂, Fe(III)/H₂O₂ and BPC/Fe(III)/H₂O₂ systems; Effects of Fe(III) concentration (b), H₂O₂ concentration (c) and BPC dosage (d) on CAF degradation in BPC/Fe(III)/H₂O₂ system; (e) CAF degradation in BPC/Fe(III)/H₂O₂ systems under different pH conditions; (f) Different pollutants degradation in BPC/Fe(III)/H₂O₂ system; (g) CAF degradation in BPC/Fe(III)/H₂O₂ system with the coexisting of anions and humic acid; (h) CAF degradation in various actual water matrices by BPC/Fe(III)/H₂O₂ system; (g) Cycle test of CAF degradation in BPC/Fe(III)/H₂O₂ system. If not specified otherwise, the BPC cocatalyst used in the experiments was BPC-30, [BPC-30]₀ = 0.04 g/L, [Fe(III)]₀ = 40.0 μM, [H₂O₂]₀ = 2.0 mM, [CAF]₀ = 10.0 mg/L, pH 4.0 and T = 25 °C.

B 1 s XPS spectra of BPC materials (Fig. 3a), which were assigned to BC₃ (~190.10 eV), BC₂O (~191.34 eV), BCO₂ (~192.20 eV) and B-O (~193.44 eV), respectively [41]. Table S4 exhibited that boron in BPC mainly existed in the form of B-C-O species (including BC₂O and BCO₂), which was attributed to the doping of boron atoms caused the rearrangement of π electrons in the carbon plane, leading to the weakening of C-C bonds and the strengthening of C-O bonds in the process of electrophilic oxygen adsorption, thus forming more BC₂O and BCO₂ functional groups [42,43].

Raman spectroscopy was used to investigate the effect of boron doping on the carbon structure of these cocatalysts. As shown in Fig. 3b, Raman spectra of PC and all BPC materials featured two distinct characteristic peaks at ~1360 cm⁻¹ and ~1590 cm⁻¹, which correspond to the D band representing the in-plane defect energy level and the G band of sp²-hybrid carbon E_{2g} vibration, respectively [44–46]. Therefore, the I_D/I_G value is able to reflect the graphitization or defect degree of the material [47]. With the increase of boron doping content in the cocatalyst (from PC to BPC-30), the I_D/I_G value gradually decreased from 1.11 to 0.87, indicating that the enrichment of boron content in favor of

enhancing the graphitization degree of porous carbon materials, thereby improving their electrical conductivity [48,49].

N₂ adsorption-desorption tests were conducted to examine the effects of boron doping on the surface characteristics and inner pore structure of as-prepared cocatalysts. Hysteresis loops appear in the relative pressure range of 0.45–0.98 in the adsorption-desorption isotherms of PC and different BPC materials (Figure S7), demonstrating that the pores in these materials are primarily mesoporous structures [50]. Once boron species were introduced, the BET specific surface area and pore volume of porous carbon materials were significantly increased (Table S6). This improvement was possibly caused by self-assembly reactions in BPC precursors, which made the materials create a three-dimensional structure with a larger specific surface area [51,52]. According to Figure S8, the most probable pore size of BPC-30 is 16.2918 nm, which is larger than the 3.9959 nm of PC. Therefore, boron doping leads to the creation of larger pore volume mesopores in materials, which increases their specific surface area and exposes additional catalytic reaction sites.

The performance of PC and different BPC materials as cocatalysts in

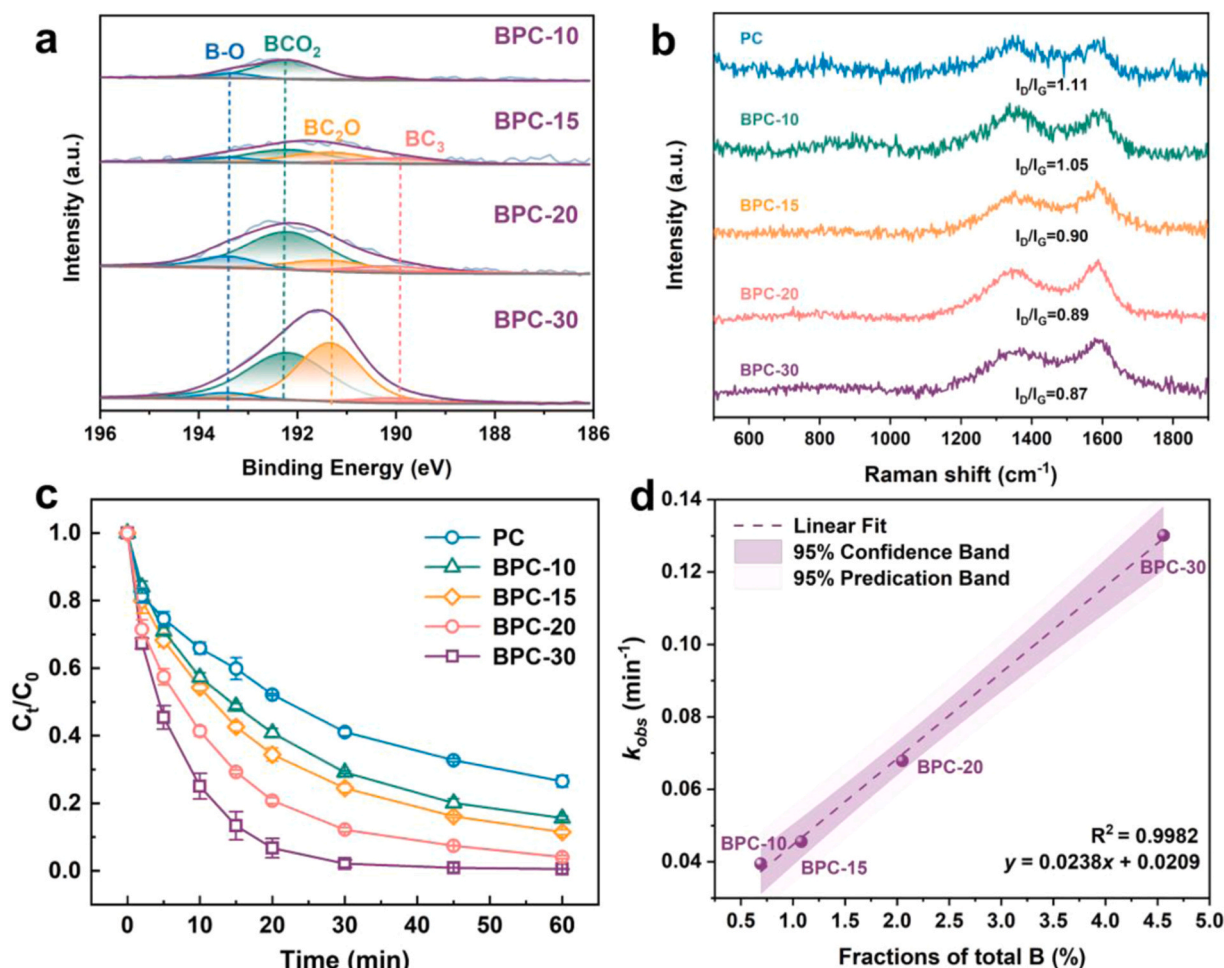


Fig. 3. (a) XPS B 1s spectra of different BPC cocatalysts; (b) Raman spectra of PC and different BPC cocatalysts; (c) CAF removal by PC/Fe(III)/H₂O₂ and different BPC/Fe(III)/H₂O₂ systems; (d) Correlation between total B content in BPC and k_{obs} of CAF degradation in different BPC/Fe(III)/H₂O₂ systems ([BPC]₀ = 0.04 g/L, [Fe(III)]₀ = 40.0 μM, [H₂O₂]₀ = 2.0 mM, [CAF]₀ = 10.0 mg/L, pH 4.0, T = 25 °C).

Fe(III)/H₂O₂ system was evaluated (Fig. 3c). The k_{obs} of CAF degradation in different BPC/Fe(III)/H₂O₂ systems rose from $(3.94 \pm 0.03) \times 10^{-2} \text{ min}^{-1}$ (BPC-10 co-catalytic system) to $(1.30 \pm 0.22) \times 10^{-1} \text{ min}^{-1}$ (BPC-30 co-catalytic system), which is linearly dependent on the amount of boron in BPC ($R^2 = 0.9982$). A similar fine linear correlation between k_{obs} and boron content in the cocatalyst ($R^2 = 0.9920$) was also obtained by using BPC prepared at different pyrolysis temperatures to enhance CAF oxidation in Fe(III)/H₂O₂ system (Figure S9). Therefore, the fact that boron doping can significantly enhance the reactivity of BPC to boost Fenton-like oxidation was demonstrated.

Taken together, boron doping has achieved appreciable effects on improving pore structure in BPC materials, which also enhances the graphitization degree and provides more reaction sites for co-catalytic reactions, leading to better performance in degrading pollutants.

3.3. Intensified Fe(III) reduction and related route analysis

Previous studies have demonstrated that there are primarily three approaches for reducing Fe(III) in a co-catalyzed Fenton-like oxidation system: (i) Cocatalyst as a reducing agent [53] or electron sacrificial agent [20,30,54] to directly reduce Fe(III), in this way, iron species mainly existed in the dissolved state; (ii) Fe(III) reacting with the cocatalyst to form a complex, then be reduced via interfacial electron transfer (the cocatalyst acts as an electron shuttle, transferring electrons from the donor to Fe(III)) [18,23,31,32], and in this case, iron species mainly exist in the surface-bound state; (iii) Enhancing the reactivity

between Fe(III) and H₂O₂ by raising the redox potential of Fe(III), thus facilitating the reduction of Fe(III) by H₂O₂ [22,29].

Iron species analysis was carried out to uncover Fe(III) reduction pathways in BPC/Fe(III)/H₂O₂ systems. As the reaction progressed, a portion of Fe(III) was converted to Fe(II) and the detected Fe(II) concentration at 5.0 min in different systems ranged from 6.54 μM (PC/Fe(III)/H₂O₂) to 7.71 μM (BPC-30/Fe(III)/H₂O₂) (Fig. 4a). Then, the free Fe(II) gradually decreased with time, which was attributed to part of iron species being bound on the BPC surface. The characteristic peak of Fe(II) in XPS Fe 2p spectra of reacted BPC-30 (Fig. 4b) obviously revealed the reactivity of BPC-30 for direct reduction of Fe(III), which demonstrated that the Fe(III)/Fe(II) transition happened on the surface of BPC-30. To further discern the differences in the Fe(III) reduction capacity of BPC materials, variations of free iron in PC/Fe(III) and different BPC/Fe(III) systems were investigated. As shown in Fig. 4c, the reduction performance of BPC for Fe(III) is undoubtedly superior to that of PC, and the reduction capacity increases as the boron level in BPC materials rises (from BPC-10 to BPC-30).

Electrochemical analysis was performed to explore the origin of boron doping for enhancing the capacity of cocatalysts to reduce Fe(III). Initially, the potential redox reactions of PC and different BPC materials in Fe(III) solution were evaluated by cyclic voltammetry (CV). As indicated by Figs. 4d and S10, the CV curves of all materials had patent cathode peaks and anode peaks, proving that the Fe(III)/Fe(II) cycle was present on the cocatalyst during scanning. The peak-to-peak separation (ΔE_p , the potential difference between the cathode peak and anode

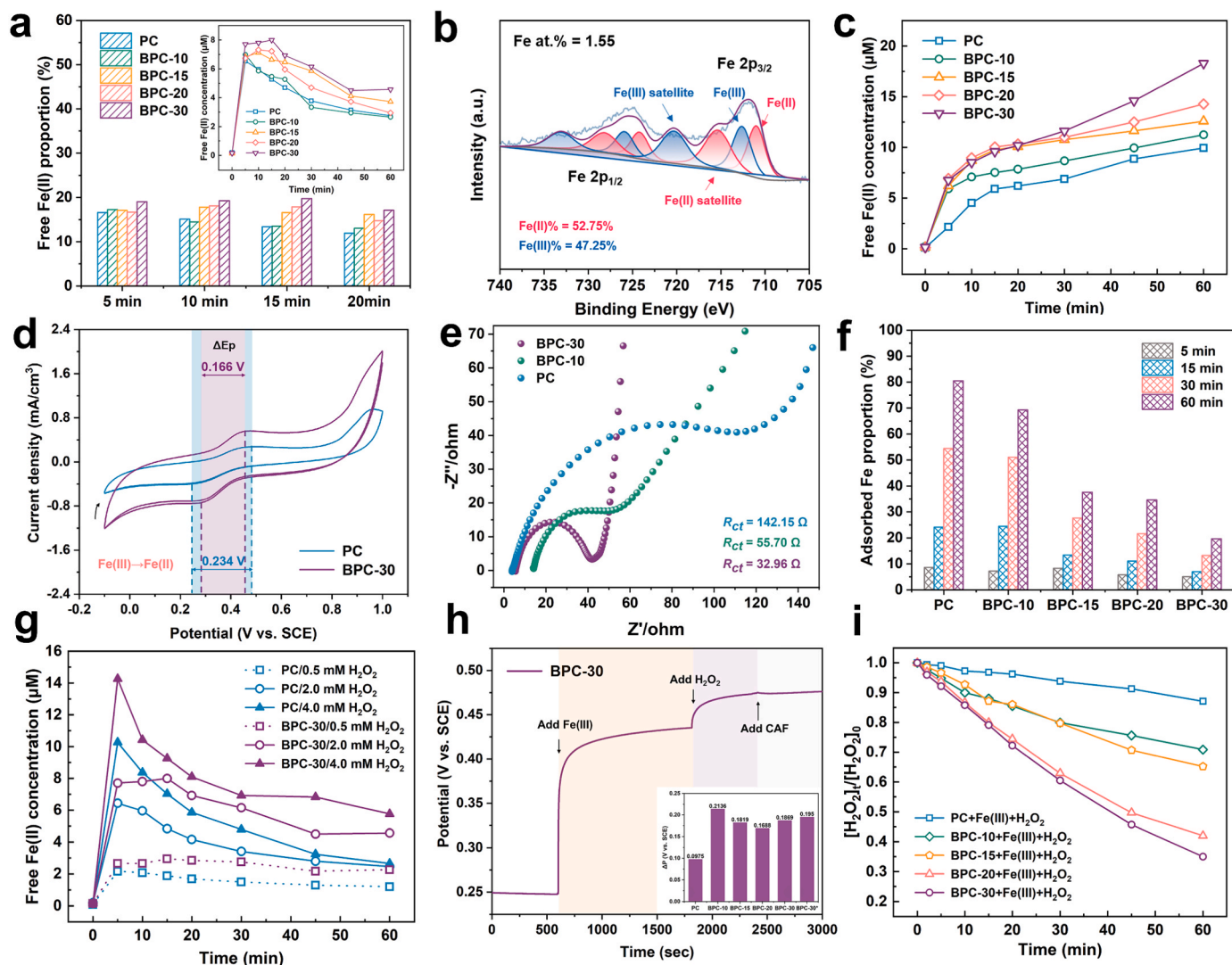


Fig. 4. (a) Variations of free Fe(II) proportion and time profiles of free Fe(II) concentration in PC/Fe(III)/H₂O₂ and different BPC/Fe(III)/H₂O₂ systems; (b) XPS Fe 2p spectra of used BPC-30; (c) Time profiles of free Fe(II) concentration in PC/Fe(III) and different BPC/Fe(III) systems; (d) CV curves on PC and BPC-30 electrodes in Fe(III) solution ([Fe(III)]₀ = 5.0 mM, [Na₂SO₄]₀ = 0.5 M, scan rate: 10 mV/s); (e) Nyquist plots of PC, BPC-10 and BPC-30; (f) Adsorbed Fe proportions with time in PC/Fe(III)/H₂O₂ and different BPC/Fe(III)/H₂O₂ systems; (g) Time profiles of free Fe(II) concentration in PC/Fe(III)/H₂O₂ and BPC-30/Fe(III)/H₂O₂ systems at different H₂O₂ concentrations; (h) Open-circuit potential curves on BPC-30 electrode after adding different substances, inset: the elevated potentials on different electrodes after adding Fe(III) for 1200 s ([Na₂SO₄]₀ = 0.5 M, [Fe(III)]_{add} = 5.0 mM, [H₂O₂]_{add} = 2.0 mM, [CAF]_{add} = 10.0 mg/L); (i) Time profiles of H₂O₂ concentration in PC/Fe(III)/H₂O₂ and different BPC/Fe(III)/H₂O₂ systems ([PC or BPC]₀ = 0.04 g/L, [Fe(III)]₀ = 40.0 μM, [H₂O₂]₀ = 2.0 mM, pH 4.0, T = 25 °C).

peak) can indicate the reversibility of electrode reaction and is typically used to evaluate the difficulty of converting Fe(III) into Fe(II) on different cocatalysts [23,29]. Compared with PC ($\Delta E_p = 0.234$ V), the ΔE_p of BPC electrodes decreased significantly. Moreover, it showed a trend toward decline with an increase in boron content, among which the ΔE_p for BPC-30 was only 0.166 V (Fig. 4d). The results indicated that boron doping reduces the reaction energy barrier of Fe(III) to Fe(II), which facilitates the reduction of Fe(III) by BPC. Electrochemical impedance spectroscopy (EIS) testing was further used to evaluate the electron transport properties of BPC materials. The semicircular diameter of the Nyquist curve represented the charge transfer resistance (R_{ct}) at the electrode-electrolyte solution interface [55,56]. As shown in Fig. 4e, the calculated R_{ct} of PC, BPC-10 and BPC-30 are 142.15 Ω , 55.70 Ω and 32.96 Ω , respectively, indicating that the increase of boron content is conducive to improving the electron conductivity of the cocatalyst. To sum up, boron doping reduces the reaction barrier for the interconversion of Fe(III) and Fe(II) on the cocatalyst, and the increase of boron content further improves the conductivity of the material,

thereby enhancing the direct reduction ability of BPC to Fe(III).

Fig. 4f displayed that the majority of iron species existed in the adsorbed state in PC and BPC-10 co-catalytic systems after a 60-min reaction, whose fraction reached 80.46% and 69.24% respectively. With increasing boron content in BPC, the fraction of free iron species rose steadily, and 80.34% of iron species were dissolved in BPC-30/Fe(III)/H₂O₂ system (Figure S11). The reduction pathway of Fe(III) in catalytic systems was related to the existence form of iron species. Considering the Fenton-like oxidation performance of different systems (Fig. 3c) and the distribution of iron species (Fig. 4f), it could be concluded that the cocatalyst-mediated interfacial electron transfer was not the main pathway for the Fe(III) reduction in BPC-30/Fe(III)/H₂O₂ system, and Fe(III) in this system was more likely to be reduced by direct reaction with BPC-30 or H₂O₂. Therefore, the enrichment of boron content in the cocatalyst induces the transition of Fe(III) reduction from the interfacial electron transfer pathway to the cocatalyst direct reduction or H₂O₂ reduction pathways.

Except for direct reduction by cocatalyst and reduction by cocatalyst-

mediated interfacial electron transfer, Fe(III) can also take electrons from H_2O_2 in the system to effect reduction (Eq. 2). However, because of its sluggish kinetics, this approach strongly limits the sustainable generation of hydroxyl radicals. Hence, some studies focus on enhancing the redox potential of iron species to accelerate the reduction of Fe(III) by H_2O_2 [22,29]. To investigate possible approaches for Fe(III) reduction by H_2O_2 in PC and BPC co-catalytic systems, the free Fe(II) concentration in the systems with various H_2O_2 concentrations was monitored. It can be seen in Fig. 4g, more free Fe(II) was detected in both PC and BPC-30 mediated systems as the H_2O_2 concentration rose (Fig. 4g), demonstrating that H_2O_2 participated in the reduction process of Fe(III). Comparing the differences of free Fe(II) concentration in PC/Fe(III)/ H_2O_2 and BPC-30/Fe(III)/ H_2O_2 systems at varying H_2O_2 concentrations, more enhancement was observed in BPC-30 mediated system when the H_2O_2 concentration was increased (Figure S12), which meant that the introduction of boron species further fostered the reaction of Fe(III) and H_2O_2 to give more free Fe(II). Results from the open-circuit potential test also supported this finding. As shown in Fig. 4h, the open-circuit potential on the BPC-30 electrode significantly increased after the addition of Fe(III) at 600 s, reaching 0.1869 V at 1800 s. The potential increase following the addition of Fe(III) in BPC electrode system was significantly higher than that in PC electrode system (inset of Fig. 4h), indicating that boron doping increased the reactivity of the cocatalyst for Fe(III), further enhancing the Fe(III) reduction pathway where H_2O_2 as the electron donor. Moreover, the H_2O_2 consumption in different BPC co-catalytic systems increased with the increase of boron content in BPC and was greater than that in PC co-catalytic system (Fig. 4i), indicating that boron in the cocatalyst promoted the effective

utilization of H_2O_2 in Fenton-like system (reducing Fe(III) or oxidizing pollutants after activation), which was consistent with the previous results of Fe(III) reduction and pollutant removal performance.

3.4. Comparison of different heteroatom-doped cocatalyst

Other porous carbon materials (i.e., NPC-30, SPC-30 and PPC-30) were also synthesized to investigate the effect of heteroatom doping on the regulation of co-catalytic activity and Fe(III) reduction routes in the corresponding systems. As shown in Fig. 5a, the doping of heteroatom did make an effect (compared with PC/Fe(III)/ H_2O_2 system in Fig. 3c), all these materials co-catalyzed Fe(III)/ H_2O_2 system could degrade pollutants effectively. The reduction mechanism of Fe(III) was then scrutinized. Fig. 5b shows all four materials exhibited the direct reduction capability to generate free Fe(II), among which BPC-30 manifested the best performance. Interestingly, more than 50% of iron species were adsorbed within 5.0 min in PPC-30 co-catalytic systems (Figs. 5c and S13), illustrating the electron-rich phosphorus site of PPC-30 promotes the surface binding of Fe(III) via electrostatic attraction [57]. The high ratio of adsorbed iron species also demonstrated that the cocatalyst-mediated interfacial electron transfer prevails for Fe(III) reduction. However, the electron transport efficiency seems unsatisfactory, causing the insufficient utilization of H_2O_2 (Fig. 5d). SPC-30 and NPC-30 co-catalytic systems shared a similar variation trend of adsorbed iron species but differed in H_2O_2 consumption (Fig. 5b-d), which was due to the different proportions of various Fe(III) reduction pathways. It was documented that N doping increases the reactivity of Fe(III) reduction by H_2O_2 , and H_2O_2 helps the interaction of Fe(III) species with

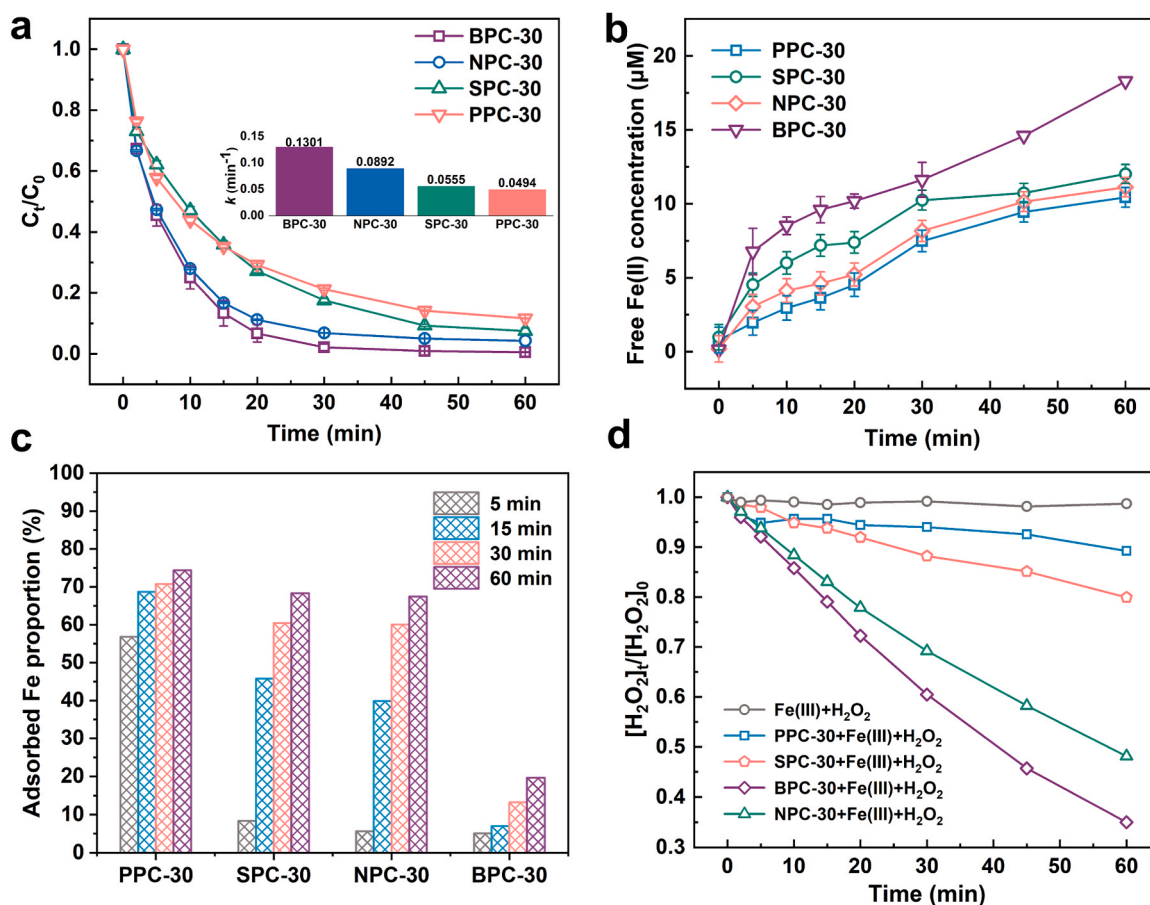


Fig. 5. (a) CAF removal and k_{obs} of CAF degradation by BPC-30, NPC-30, SPC-30 and PPC-30 co-catalyzed Fe(III)/ H_2O_2 systems; (b) Time profiles of free Fe(II) concentration in Fe(III) solutions reduced by BPC-30, NPC-30, SPC-30 and PPC-30 co-catalyzed Fe(III)/ H_2O_2 systems; (c) Adsorbed Fe proportions with time in BPC-30, NPC-30, SPC-30 and PPC-30 co-catalyzed Fe(III)/ H_2O_2 systems; (d) Variations of H_2O_2 concentration in Fe(III)/ H_2O_2 and BPC-30, NPC-30, SPC-30 and PPC-30 co-catalyzed Fe(III)/ H_2O_2 systems. If not specified otherwise, [cocatalyst]₀ = 0.04 g/L, [Fe(III)]₀ = 40.0 μM, [H_2O_2]₀ = 2.0 mM, pH 4.0, T = 25 °C.

the N-doped cocatalyst to induce interfacial electron transfer [23]. Evidently, the doping of boron in boosting the co-catalytic oxidation performance of Fe(III)/H₂O₂ system notably outperforms other dopants (Fig. 5a), which was credited to the switch in the conversion route and existence form of iron species enhanced the effective activation of H₂O₂ by improving the mass transfer process (Fig. 5d). To sum up, heteroatom doping steers the co-catalytic properties of porous carbon materials and breeds distinctive Fe(III) reduction routes. Bearing the robust Fe(III) reduction efficiency, B-doped cocatalysts possess greater development potential.

3.5. DFT calculations and distinguish of active boron species

DFT calculations were performed to emulate the charge transfer between different boron species (B-O, BC₂O, BCO₂, BC₃) and Fe(OH)₂⁺ (the prime Fe(III) species at pH 4.0, 64.04%, Figure S15) on the molecular scale, and the corresponding interaction configurations were displayed in Figs. 6a and S16.

Firstly, the differential charge distribution diagram provided a clear visualization of the electron accumulation and loss distribution across Fe(OH)₂⁺ on different BPC configurations (Fig. 6b), which was then quantitatively assessed by the Bader charge. In comparison to other models, Fe(III) accumulated more electrons (1.919 e) from BCO₂ configuration (Figs. 6c and S17), alluding to BCO₂ species on BPC may be more reactive for Fe(III) reduction. Similarly, the total electron loss of all C atoms and charge depletion in the B atom on the BCO₂ model run ahead among all configurations (Figs. 6d and S17), implying that the B and C atoms within this model were more likely to relinquish electrons, thereby reducing more Fe(III).

Next, the projected density of states (PDOS) was analyzed to further determine the main role of BCO₂ species. The d-band centers of Fe 3d orbitals in BCO₂ + Fe(OH)₂⁺, BC₂O + Fe(OH)₂⁺, B-O + Fe(OH)₂⁺, and BC₃ + Fe(OH)₂⁺ models are located at -0.8801, -0.9087, -1.0261 and -1.0418 eV, respectively (Fig. 6e). Compared with other models, the d-

band center of the Fe atom in BCO₂ + Fe(OH)₂⁺ was closer to the Fermi level, which indicated that BCO₂ species were more suitable to serve as the electronic porters [58]. Figs. 6f and S17c depict the adsorption energy (*E*_{ads}) of Fe(OH)₂⁺ attached to graphene (represents PC) and four kinds of boron-containing models. Strong binding of Fe(III) on BC₃ (*E*_{ads} = -2.747 eV) covered active boron sites, which led to its inactivation for electron transfer. On the other hand, the relatively weaker binding affinity of Fe(III) on B-O (*E*_{ads} = -1.640 eV), BC₂O (*E*_{ads} = -1.855 eV) and C-C/C=C (*E*_{ads} = -1.894 eV) would impede charge exchange for Fe(II) regeneration [59]. Draw on the above discussions, the moderate adsorption energy of Fe(OH)₂⁺ on BCO₂ (*E*_{ads} = -2.353 eV) enables BCO₂ as the pioneer to sustainably transfer electrons to Fe(III) without poisoning, which was also in line with the fact that the proportion of adsorbed Fe species shrunken with the increase of boron content (BCO₂ is the main boron species, Figs. 3a and 4f). This further substantiated that BCO₂ is the primary active boron species in BPC.

3.6. Identification of active reactive species and dominant oxidation mechanism

Electron spin resonance (ESR) test, quenching experiment and probe experiment were carried out to qualitatively and quantitatively analyze the reactive species produced in BPC/Fe(III)/H₂O₂ system, and further determine the dominant oxidation mechanism.

Figs. 7a-b and S18-S19 displayed the ESR spectra for detecting •OH, HO₂[•]/O₂^{•-} and ¹O₂ using DMPO and TEMP as trapping agents. BPC-30/H₂O₂ system only detected faint signals of the DMPO-HO• and TEMP-¹O₂ adducts, illustrating that BPC-30 alone has a limited capacity to activate H₂O₂. Evident DMPO-HO•, DMPO-HO₂[•]/O₂^{•-} and TEMP-¹O₂ characteristic signals were all observed in the ESR spectra of Fe(III)/H₂O₂ and BPC-30/Fe(III)/H₂O₂ systems, indicating that these three ROS were all generated during the reaction. Notably, the DMPO-HO• and DMPO-HO₂[•]/O₂^{•-} signals in ESR spectra significantly increased after BPC-30 was added to Fe(III)/H₂O₂ system, demonstrating that BPC-30

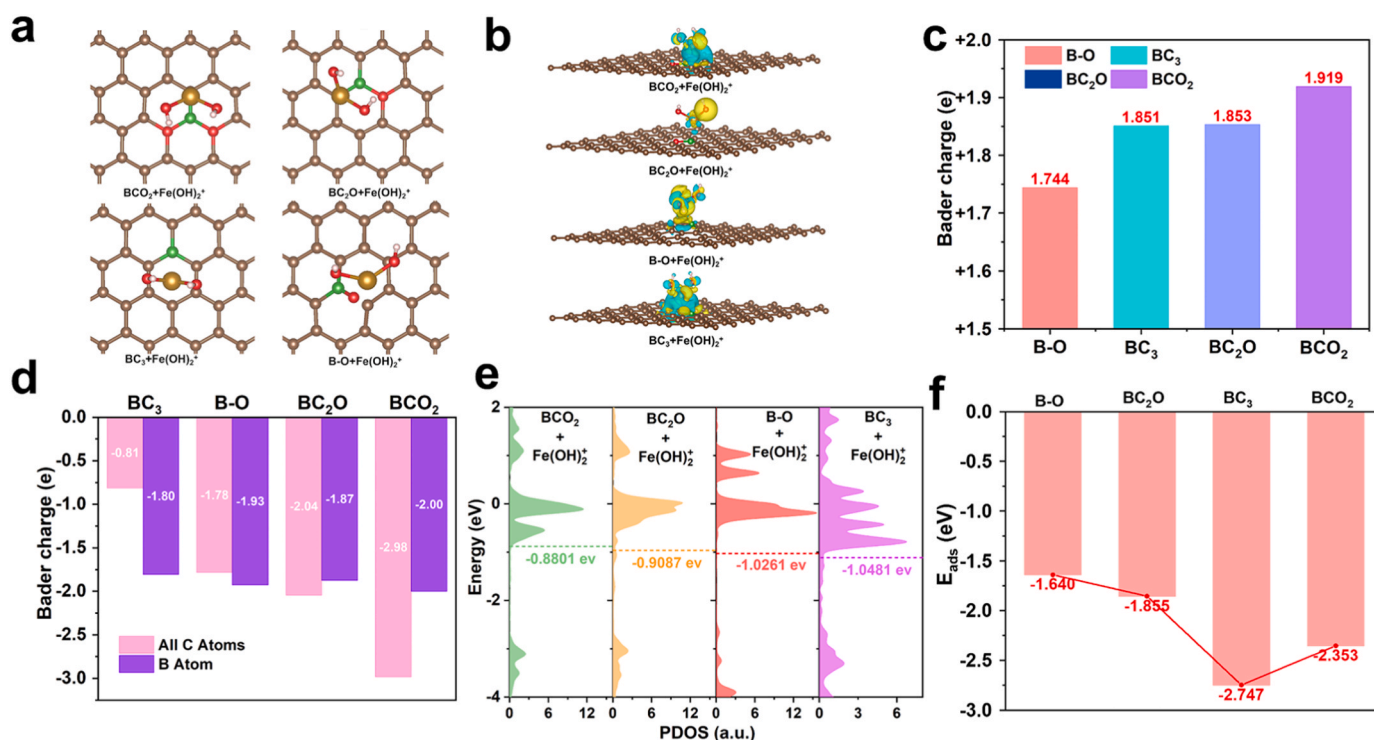


Fig. 6. (a) Optimized calculation models for Fe(OH)₂⁺ on different boron species (top view); (b) Charge density difference diagrams for Fe(OH)₂⁺ on different boron species, the electron accumulation and depletion regions are indicated by cyan and yellow, respectively (isosurface = 0.0025); (c) Bader charge of Fe atoms in Fe(OH)₂⁺ on different boron species; (d) Bader charge of B and all C atoms on different configurations; (e) Comparison of PDOS of Fe atoms in different calculation models; (f) Adsorption energy values of Fe(OH)₂⁺ on different boron sites.

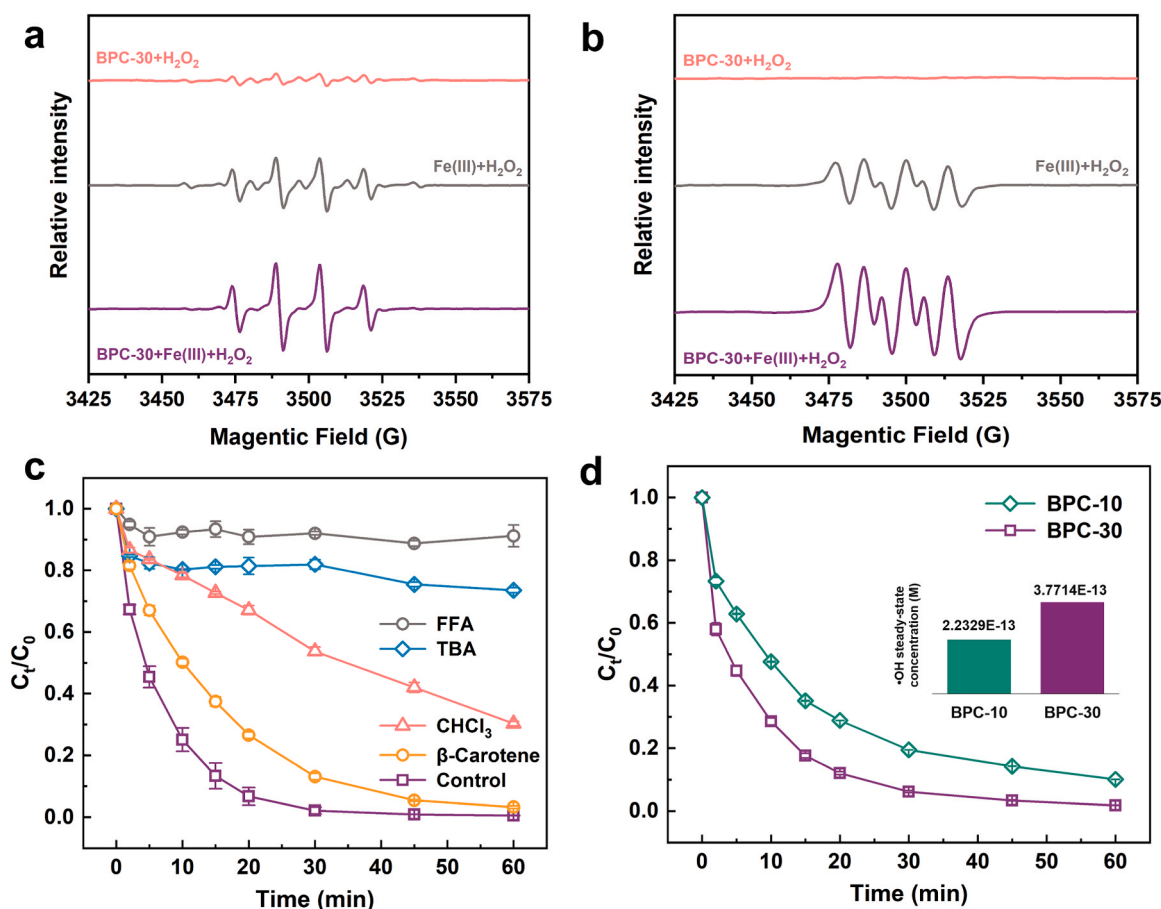


Fig. 7. (a) ESR spectra for detection of DMPO-HO•; (b) DMPO-HO₂•/O₂•⁻; (c) Effects of various quenchants on CAF removal efficiency in BPC-30/Fe(III)/H₂O₂ system ([BPC-30] = 0.04 g/L, [Fe(III)]₀ = 40.0 μM, [H₂O₂]₀ = 2.0 mM, [CAF]₀ = 10.0 mg/L, [quencher]₀ = 20.0 mM, pH 4.0, and T = 25 °C); (d) Degradation of NB in BPC-10/Fe(III)/H₂O₂ and BPC-30/Fe(III)/H₂O₂ systems, inset: the calculated •OH steady-state concentrations ([BPC] = 0.04 g/L, [Fe(III)]₀ = 40.0 μM, [H₂O₂]₀ = 2.0 mM, [NB]₀ = 10.0 mg/L, pH 4.0 and T = 25 °C).

promoted Fe(III) reduction by H₂O₂ and produced more HO₂•/O₂•⁻ through Eq. 2, as well as, sped up the regeneration of Fe(II) and then activated H₂O₂ to produce more •OH. In addition, the intensity of DMPO-HO• adduct in BPC-30/Fe(III)/H₂O₂ system was evidently higher than that of PC/Fe(III)/H₂O₂ system (Figure S19a), confirming that boron doping elevates the activity of porous carbon materials for enhancing the oxidation ability of Fe(III)/H₂O₂ system.

To further examine the oxidation contribution of different ROS in pollutant degradation, quenching experiments were carried out. Tert-butanol (TBA, $k_{\text{TBA}+\bullet\text{OH}} = (3.8-7.6) \times 10^8 \text{ M}^{-1}\cdot\text{s}^{-1}$) [12,60], chloroform (CHCl₃, $k_{\text{CHCl}_3+\text{HO}_2\bullet/\text{O}_2\bullet^-} = 3 \times 10^{10} \text{ M}^{-1}\cdot\text{s}^{-1}$) [61] and β-carotene ($k_{\beta\text{-carotene}+\bullet\text{OH}} = (2.0-3.0) \times 10^9 \text{ M}^{-1}\cdot\text{s}^{-1}$) [26,62] were used as the exclusive inhibitor of •OH, HO₂•/O₂•⁻ and ¹O₂ respectively, while furfuryl alcohol (FFA) was used to quench ¹O₂ and •OH ($k_{\text{FFA}+\bullet\text{OH}} = 1.2 \times 10^8 \text{ M}^{-1}\cdot\text{s}^{-1}$, $k_{\text{FFA}+\text{O}_2\bullet^-} = 1.5 \times 10^{10} \text{ M}^{-1}\cdot\text{s}^{-1}$) [63–66]. As shown in Fig. 7c, the addition of β-carotene only slightly slowed the degradation of CAF, and the removal rate still reached 96.72% after 60 min, indicating that the non-radical ¹O₂ oxidation contributed little to CAF elimination. After adding TBA and CHCl₃, the CAF removal rate dropped to 69.68% and 26.42%, respectively. The more pronounced inhibitory effect of TBA suggested that •OH is more crucial to the degradation of CAF. The elimination rate of CAF was reduced further with the addition of FFA, and the capacity to oxidize CAF was almost completely hindered, which indicated that ¹O₂ was also engaged in the oxidation process of CAF.

Next, the presence of high-valent iron species in BPC-30/Fe(III)/H₂O₂ system was examined. Methylphenyl sulfoxide (PMSO) can react with high-valence metal species to form the corresponding

methylphenyl sulfone (PMSO₂) [67–70], which is always used as a probe compound for the detection of high-valent iron species. However, no conversion of PMSO to PMSO₂ was observed in BPC-30/Fe(III)/H₂O₂ and Fe(III)/H₂O₂ systems (Figure S20), demonstrating that the above systems did not generate high-valent iron species during the reaction. The contribution of the electron transfer pathway (ETP) was evaluated by chronopotentiometry [71–73]. As shown in Fig. 4h, after CAF was added at 2400 s, the potential did not change significantly, indicating that the ETP pathway could not cause effective oxidation of CAF [71, 74]. In conclusion, the degradation of CAF in BPC/Fe(III)/H₂O₂ system was mostly unaffected by the non-radical oxidation pathways (¹O₂, high-valent iron species, and ETP); Free radical pathway is the predominant oxidation mechanism, and •OH plays a vital role in the degradation of CAF.

The •OH steady-state concentrations in different BPC/Fe(III)/H₂O₂ systems were determined using nitrobenzene (NB) as the probe ($k_{\text{OH}, \text{NB}} = 3.9 \times 10^9 \text{ M}^{-1}\cdot\text{s}^{-1}$) [75]. As shown in Fig. 7d, BPC-10 and BPC-30 co-catalytic Fe(III)/H₂O₂ systems removed more than 90% of NB within 60 min with the k_{obs} values of $(5.23 \pm 0.02) \times 10^{-2} \text{ min}^{-1}$ and $(8.83 \pm 0.11) \times 10^{-2} \text{ min}^{-1}$, respectively. As a result, the corresponding •OH steady-state concentrations were calculated to be $(2.23 \pm 0.01) \times 10^{-13} \text{ M}$ and $(3.77 \pm 0.05) \times 10^{-13} \text{ M}$, respectively. It was evident that boron doping improved the effectiveness of pollutant degradation by promoting the formation of •OH in the system.

3.7. Application trial of BPC/Fe(III)/H₂O₂ system in water treatment

Effectively eliminating organic micropollutants, which are omnipresent in surface waters worldwide, remains a harsh challenge in actual water treatment [76,77]. The fascinating co-catalytic performance of BPC encouraged us to further realize its device integration for micro-polluted water decontamination. Thus, a continuous flow catalytic reactor based on a water-purification membrane was constructed. Specifically, the material was loaded on a polyethersulfone (PES) membrane by simple vacuum filtration and another PES membrane was attached to its surface to prevent it from dispersing into the solution, thus forming a stable sandwich-shaped BPC membrane (Fig. 8a). The obtained membrane was then assembled with an ultrafiltration cup to form a membrane filter (Fig. 8b). Fig. 8c displayed the final continuous flow device, in which a peristaltic pump was used to inject the pollutant stock solution containing Fe(III) and H₂O₂ while allowing for control of the water flux. A continuous degradation experiment of CAF was conducted to examine the application potential of this device. After optimizing the reaction conditions (treatment capacity: 0.3 L/h), the removal efficiency of CAF after a single flow-through treatment reached over 87% (Fig. 8d). Most crucially, the removal efficiency remained almost constant despite the continuous treatment of 20.0 L sewage, which further proved the excellent performance of the BPC co-catalytic filter and demonstrated its feasibility for long-term operation. Due to its high removal efficiency, stability and low cost, we consider it to be an ideal water purification device for treating micropollutants.

4. Conclusion

In this study, boron-doped porous carbon (BPC) was prepared

through a facile method for constructing a novel co-catalytic oxidation system. A small amount of BPC (0.04 g/L) significantly enhanced the oxidation performance of Fe(III)/H₂O₂ system, which realized water decontamination via •OH-dominated radical pathway. The doping of boron not only optimized the pore structure of the material but also enhanced its electron transfer ability. Besides, boron doping improved the redox potential of Fe(III) and reduced the reaction barrier of Fe(III)/Fe(II) cycle in BPC/Fe(III)/H₂O₂ system. Interestingly, the Fe(III) reduction pathway was found to be regulated by adjusting the amount or type of heteroatom. The increase of boron species in the material enhanced Fe(III) reduction by H₂O₂ and direct electron supply from the cocatalyst, differing from P, N, and S species. In addition, BCO₂ was confirmed as the active species on BPC, and the activity origin of BCO₂ was further unveiled by DFT modelling. Importantly, the co-catalytic membrane developed from BPC worked well in the flow-through process for micro-polluted water purification. Our research supplies novel insights into the co-catalytic mechanism of heteroatom-doped carbon-based Fenton-like technology.

CRediT authorship contribution statement

Huanjing Zhang: Investigation, Methodology, Formal analysis, Computation, Writing -original draft. **Cheng Chen:** Conceptualization, Investigation, Methodology, Formal analysis, Supervision, Writing -original draft, Writing - review & editing. **Muke Lin:** Investigation, Formal analysis. **Lingzhi Zhou:** Software, Computation. **Hailing Wen:** Investigation, Validation. **Tao Zhong:** Validation, Software. **Huinan Zhao:** Validation. **Shuanghong Tian:** Validation, Supervision. **Chun He:** Resources, Supervision, Funding Acquisition, Writing - review & editing.

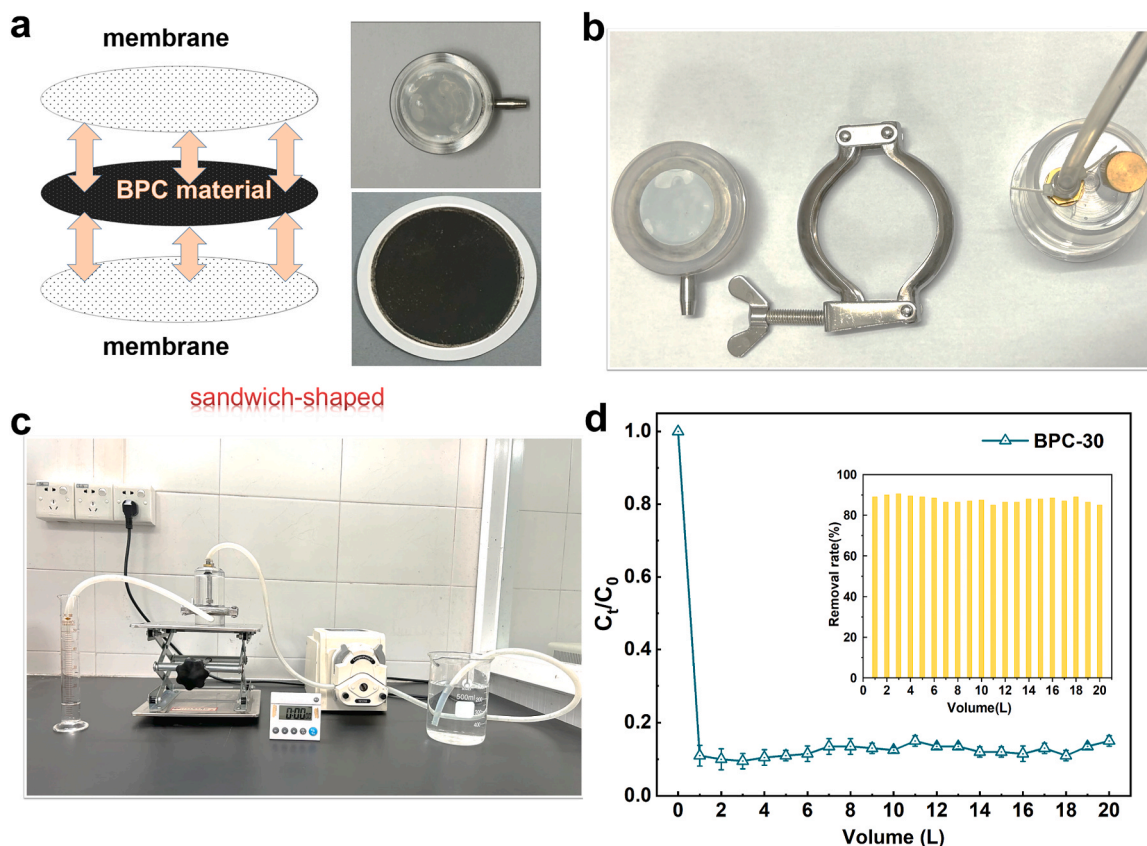


Fig. 8. (a) Schematic diagram and actual picture of co-catalytic filtration membrane equipped with BPC material; (b) Top view of core components of the membrane reactor; (c) Actual operation photograph of continuous degradation of CAF in the flow-through membrane reactor; (d) Continuous degradation of CAF by BPC/Fe(III)/H₂O₂ system in a flow-through membrane reactor, inset: removal rate ([BPC] = 0.10 g/L, [Fe(III)]₀ = 80.0 μM, [H₂O₂]₀ = 2.0 mM, [CAF]₀ = 2.0 mg/L, pH 4.0 and T = 25 °C, treatment capacity: 0.3 L/h).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2023.123535.

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